

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-313549

(43)Date of publication of application : 06.11.2003

(51)Int.Cl.

C09K 11/08

C09K 11/59

C09K 11/64

C09K 11/66

(21)Application number : 2002-122050

(71)Applicant : SUMITOMO CHEM CO LTD

(22)Date of filing : 24.04.2002

(72)Inventor : ONO KEIJI
MIYAZAKI SUSUMU

(54) PHOSPHOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a phosphor having high luminance after exposed to a plasma, and to provide a phosphor paste containing the phosphor.

SOLUTION: The phosphor contains a fluorescent material comprising a compound represented by the composition formula: $mM1O-nM2O-2M3O_2$ (wherein, M1 is two or more kinds selected from the group consisting of Ca, Sr and Ba, or Ca or Ba; M2 is one or more kinds selected from the group consisting of Mg and Zn; M3 is one or more kinds selected from the group consisting of Si and Ge; m is 0.5-3.5; and n is 0.5-2.5), and one or more kinds of activators selected from the group consisting of Eu and Mn as a first component, and a fluorescent material comprising an aluminate as a second component. The phosphor paste comprises the phosphor, a solvent and a binder.

LEGAL STATUS

[Date of request for examination]

24.03.2005

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19) 日本国特許庁 (J P)

(12) 公 開 特 許 公 報 (A)

(11) 特許出願公開番号
特開2003-313549
(P2003-313549A)

(43) 公開日 平成15年11月6日 (2003. 11. 6)

(51) Int.Cl. ⁷	識別記号	F I	テマコード* (参考)
C 0 9 K 11/08		C 0 9 K 11/08	J 4 H 0 0 1
11/59	C P R	11/59	C P R
11/64	C P T	11/64	C P T
11/66	C P M	11/66	C P M

審査請求 未請求 請求項の数9 O L (全 5 頁)

(21) 出願番号 特願2002-122050(P2002-122050)

(22) 出願日 平成14年4月24日 (2002. 4. 24)

(71) 出願人 000002093

住友化学工業株式会社

大阪府大阪市中央区北浜4丁目5番33号

(72) 発明者 大野 慶司

茨城県つくば市北原6 住友化学工業株式
会社内

(72) 発明者 宮崎 進

茨城県つくば市北原6 住友化学工業株式
会社内

(74) 代理人 100093285

弁理士 久保山 隆 (外2名)

最終頁に続く

(54) 【発明の名称】 蛍光体

(57) 【要約】

【課題】 プラズマ曝露後の輝度が高い蛍光体および該蛍光体を含有してなる蛍光体ペーストを提供する。

【解決手段】 第一の成分として、組成式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ (式中の M^1 は Ca、Sr および Ba からなる群より選ばれる2種以上または Ca または Ba であり、 M^2 は Mg および Zn からなる群より選ばれる1種以上であり、 M^3 は Si および Ge からなる群より選ばれる1種以上であり、 m は 0.5 以上 3.5 以下であり、 n は 0.5 以上 2.5 以下である。) で表される化合物と Eu、Mn からなる群より選ばれる1種以上の付活剤からなる蛍光物質と、第二の成分としてアルミン酸塩からなる蛍光物質とを含む蛍光体。前記の蛍光体と溶剤とバインダーとを含む蛍光体ペースト。

(2)

【特許請求の範囲】

【請求項1】第一の成分として、組成式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはCaまたはBaであり、 M^2 はMgおよびZnからなる群より選ばれる1種以上であり、 M^3 はSiおよびGeからなる群より選ばれる1種以上であり、mは0.5以上3.5以下であり、nは0.5以上2.5以下である。）で表される化合物とEu、Mnからなる群より選ばれる1種以上の付活剤からなる蛍光物質と、第二の成分としてアルミン酸塩からなる蛍光物質とを含むことを特徴とする蛍光体。

【請求項2】第一の成分／第二の成分の重量比が5／9.5～9.5／5である請求項1記載の蛍光体。

【請求項3】第一の成分が組成式 $(M^1)_a(M^2)_b(M^3)_cO_6$ （式中の M^1 、 M^2 および M^3 は前記と同じ意味を有し、aは0以上0.5以下であり、bは0以上0.5以下であり、 $0 < a + b$ である。）で表される組成を有する蛍光物質である請求項1または2に記載の蛍光体。

【請求項4】第一の成分が組成式 $Ca_{1-c-d}Sr_cEu_dMgSi_2O_6$ （式中のcは0以上0.1以下であり、dは0より大きく0.1以下である。）で表される組成を有する蛍光物質である請求項1～3のいずれかに記載の蛍光体。

【請求項5】第二の成分が組成式 $p(M^4)_eEu_fO \cdot q(M^5)_iMn_jO \cdot rAl_2O_3$ （式中の M^4 はCa、SrおよびBaからなる群より選ばれる1種以上であり、 M^5 はMgおよびZnからなる群より選ばれる1種以上であり、pは0.5以上1.5以下であり、qは0.5以上1.5以下であり、rは4.5以上5.5以下であり、eは0より大きく0.5以下であり、fは0より大きく0.1以下である。）で表される組成を有する蛍光物質である請求項1～4のいずれかに記載の蛍光体。

【請求項6】第二の成分が組成式 $Ba_{1-g}Eu_gMgAl_{10}O_{17}$ （式中のgは0より大きく0.3以下である。）で表される組成を有する蛍光物質である請求項1～5のいずれかに記載の蛍光体。

【請求項7】第一の成分と第二の成分のうちいずれかの平均一次粒子径がもう一方の平均一次粒子径の5倍以下である請求項1～6のいずれかに記載の蛍光体。

【請求項8】真空紫外線励起発光素子用である請求項1～7のいずれかに記載の蛍光体。

【請求項9】請求項1～8のいずれかに記載の蛍光体と溶剤とバインダーとを含むことを特徴とする蛍光体ペースト。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は蛍光体および蛍光体ペーストに関する。

【0002】

【従来の技術】蛍光体は、蛍光灯、夜光表示、X線検査装置、CRT、真空紫外線励起発光素子などに用いられている。プラズマディスプレイ（PDP）や希ガスランプなどの真空紫外線励起発光素子用であり、真空紫外線によって励起され発光する蛍光体はすでに知られている。例えば、アルミン酸塩蛍光体である $BaMgAl_{10}O_{17}:Eu$ が青色蛍光体として、ケイ酸塩蛍光体である $CaMgSi_2O_6:Eu$ が青色蛍光体として、 $Zn_2SiO_4:Mn$ が緑色蛍光体として、ホウ酸塩蛍光体である $(Y,Gd)BO_3:Eu$ が赤色蛍光体として実用化されており、PDPや希ガスランプ等の真空紫外線励起発光素子用に用いられている。

【0003】しかしながら、真空紫外線励起発光素子は希ガス中の放電によりプラズマを発生させ、プラズマから放射される真空紫外線を蛍光体に照射して蛍光体を励起し、蛍光体から放射される可視光により発光するので、蛍光体はプラズマに曝露され、プラズマ曝露後の蛍光体の輝度が低くなるという問題があった。

【0004】

【発明が解決しようとする課題】本発明の目的は、プラズマ曝露後の輝度が高い蛍光体および該蛍光体を含有してなる蛍光体ペーストを提供することにある。

【0005】

【課題を解決するための手段】本発明者らは、かかる状況下、上記の課題を解決すべく鋭意研究を重ねた結果、アルミン酸塩からなる蛍光物質と特定の組成を有するケイ酸塩からなる蛍光物質とを共に含む蛍光体は、プラズマ曝露後の輝度が高いことを見出し、本発明を完成するに至った。

【0006】すなわち本発明は、第一の成分として、組成式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ （式中の M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはCaまたはBaであり、 M^2 はMgおよびZnからなる群より選ばれる1種以上であり、 M^3 はSiおよびGeからなる群より選ばれる1種以上であり、mは0.5以上3.5以下であり、nは0.5以上2.5以下である。）で表される化合物とEu、Mnからなる群より選ばれる1種以上の付活剤からなる蛍光物質と、第二の成分としてアルミン酸塩からなる蛍光物質とを含む蛍光体を提供する。また本発明は、上記記載の蛍光体と溶剤とバインダーとを含む蛍光体ペーストを提供する。

【0007】

【発明の実施の形態】以下に本発明について詳しく説明する。本発明の蛍光体は、組成式 $mM^1O \cdot nM^2O \cdot 2M^3O_2$ で表される化合物に付活剤としてEu、Mnからなる群より選ばれる1種以上が含有されてなる蛍光物質（以下「蛍光物質A¹」ということがある。）を含む。前記式中の M^1 はCa、SrおよびBaからなる群より選ばれる2種以上またはCaまたはBaである。 M^2 は

(3)

3

MgおよびZnからなる群より選ばれる1種以上である。M³はSiおよびGeからなる群より選ばれる1種以上である。mは0.5以上3.5以下であり、nは0.5以上2.5以下である。m、nが上記範囲外であるとプラズマ曝露後の蛍光体の輝度が低くなる。

【0008】蛍光物質A¹としては、組成式(M¹_{1-a}Eu_a)(M²_{1-b}Mn_b)M³2O₆(式中のM¹、M²およびM³は前記と同じ意味を有し、aは0以上0.5以下であり、bは0以上0.5以下であり、0<a+bである。)で表される組成を有する蛍光物質が好ましく、さらに好ましくは、組成式Ca_{1-c-d}Sr_cEu_dMgSi₂O₆(式中のcは0以上0.1以下であり、dは0より大きく0.1以下である。)で表される組成を有する蛍光物質である。

【0009】本発明の蛍光体には、上記A¹の他に、アルミン酸塩からなる蛍光物質(以下「蛍光物質B¹」ということがある。)を含む。アルミン酸塩からなる蛍光体であれば特に限定されないが、組成式p(M⁴_{1-e}Eu_e)O·q(M⁵_{1-f}Mn_f)O·rAl₂O₃(式中のM⁴はCa、SrおよびBaからなる群より選ばれる1種以上であり、M⁵はMgおよびZnからなる群より選ばれる1種以上であり、pは0.5以上1.5以下であり、qは0.5以上1.5以下であり、rは4.5以上5.5以下であり、eは0より大きく0.5以下であり、fは0より大きく0.1以下である。)で表される組成を有する蛍光物質(以下「蛍光物質B²」ということがある。)が好ましく、組成式Ba_{1-g}Eu_gMgAl₁₀O₁₇(式中のgは0より大きく0.3以下である。)で表される組成を有する蛍光物質がさらに好ましい。

【0010】本発明の蛍光体において、蛍光物質A¹/蛍光物質B¹の重量比は5/95~95/5の範囲が好ましく、20/80~90/10の範囲がさらに好ましく、30/70~85/15の範囲がさらに好ましい。蛍光物質A¹/蛍光物質B¹の重量比が5/95より大きい場合または95/5より小さい場合は、プラズマ曝露後の輝度が低くなるおそれがある。

【0011】また、蛍光物質A¹と蛍光物質B¹のうちいずれかの蛍光物質の平均一次粒子径がもう一方の蛍光物質の平均一次粒子径の5倍以下であることが好ましい。

【0012】次に本発明の蛍光体の製造方法について説明する。本発明の蛍光体は、蛍光物質A¹と蛍光物質B¹を混合することにより得ることができる。混合する方法としては、特に限定されないが、通常工業的に用いられている攪拌法、ボールミル法、三本ロールミル法等を例示することができる。また、A¹とB¹以外の蛍光体を混合しても良い。

【0013】ここで、蛍光物質A¹は、例えば、金属化合物の混合物であって、焼成により蛍光物質A¹となりうる混合物を焼成することにより製造することができる。蛍光物質A¹を製造するためのカルシウム源、スト

4

ロンチウム源、バリウム源としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうる化合物かまたは高純度(99.9%以上)の酸化物が使用できる。マグネシウム源、亜鉛源としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。ケイ素源、ゲルマニウム源としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。付活剤となるユーロピウム、マンガンを含む原料としては、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99%以上)の酸化物が使用できる。

【0014】蛍光物質A¹は上記化合物を所定の組成となるように秤量し配合し、混合して焼成することにより製造することができる。これらの化合物の混合には通常工業的に用いられているボールミル、V型混合機、または攪拌装置等を用いることができる。混合した後、例えば1000℃から1500℃の温度範囲にて1~100時間焼成することにより本発明における蛍光物質A¹が得られる。水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうる化合物を用いた場合、本焼成の前に、例えば600℃から900℃の温度範囲にて仮焼することも可能である。

【0015】蛍光物質A¹を製造するための焼成雰囲気としては、特に限定されるものではないが、例えば水素を0.1~10体積%含む窒素やアルゴン等の還元性雰囲気中で焼成することが好ましい。また仮焼の雰囲気は大気雰囲気、還元性雰囲気のいずれでもよい。また、反応を促進するために、適量のフラックスを添加してもよい。

【0016】さらに、上記方法にて得られる蛍光物質A¹を、例えばボールミル、ジェットミル等を用いて粉砕することができる。また、洗浄、分級することができる。得られた蛍光物質A¹の結晶性を高めるために、再焼成を行うこともできる。

【0017】次に、本発明における蛍光物質B¹の製造方法について説明する。蛍光物質B¹の製造方法は特に限定されないが、金属化合物の混合物であって、焼成によりアルミン酸塩からなる蛍光物質となりうる混合物を焼成することにより製造することができる。例えば、蛍光物質B¹のうちで好ましい組成を有する蛍光物質B²を製造するための金属化合物の混合物を得るには、バリウム源として、高純度(99%以上)の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度(99.9%以上)の酸化物が使用できる。マグネシウム源としては、

(4)

5

高純度（99%以上）の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度（99%以上）の酸化物が使用できる。アルミニウム源としては、高純度（99%以上）の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度（99%以上）の酸化物が使用できる。付活剤となるユーロピウムを含む原料としては、高純度（99%以上）の水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうるものかまたは高純度（99%以上）の酸化物が使用できる。上記化合物を所定の組成となるように秤量し、混合することにより金属化合物の混合物が得られる。混合には通常工業的に用いられているボールミル、V型混合機、または攪拌装置等を用いることができる。

【0018】金属化合物の混合物を、例えば1000℃から1500℃の温度範囲にて1～100時間焼成することにより蛍光物質B¹が得られる。水酸化物、炭酸塩、硝酸塩、ハロゲン化物、シュウ酸塩など高温で分解し酸化物になりうる化合物を用いた場合、本焼成の前に、例えば600℃から900℃の温度範囲にて仮焼することも可能である。

【0019】蛍光物質B¹を製造するための焼成雰囲気としては、特に限定されるものではないが、例えば水素を0.1～10体積%含む窒素やアルゴン等の還元性雰囲気中で焼成することが好ましい。また仮焼の雰囲気は大気雰囲気、還元性雰囲気のいずれでもよい。また、反応を促進するために、適量のフラックスを添加してもよい。

【0020】さらに、上記方法にて得られる蛍光物質B¹を、例えばボールミル、ジェットミル等を用いて粉砕することができる。また、洗浄、分級することができる。得られる蛍光体の結晶性を高めるために、再焼成を行うこともできる。

【0021】次に、本発明の蛍光体ペーストについて説明する。本発明の蛍光体ペーストは、本発明の蛍光体と溶剤とバインダーを含み、従来の蛍光体ペーストと同様に用いることができ、焼成すると本発明の蛍光体が残存する蛍光体ペーストである。

【0022】本発明の蛍光体ペーストは公知のバインダーおよび溶剤を用い、公知の方法により製造することができる。例えば、蛍光物質A¹と蛍光物質B¹とバインダーと溶剤とを、ボールミルや三本ロールミル等を用いて混合することにより、得ることができる。

【0023】バインダーとしては、セルロース系樹脂（エチルセルロース、メチルセルロース、ニトロセルロース、アセチルセルロース、セルロースプロピオネート、ヒドロキシプロピルセルロース、ブチルセルロース、ベンジルセルロース、変性セルロースなど）、アクリル系樹脂（アクリル酸、メタクリル酸、メチルアクリ

6

レート、メチルメタクリレート、エチルアクリレート、エチルメタクリレート、プロピルアクリレート、プロピルメタクリレート、イソプロピルアクリレート、イソプロピルメタクリレート、n-ブチルアクリレート、n-ブチルメタクリレート、tert-ブチルアクリレート、tert-ブチルメタクリレート、2-ヒドロキシエチルアクリレート、2-ヒドロキシエチルメタクリレート、2-ヒドロキシプロピルアクリレート、2-ヒドロキシプロピルメタクリレート、ベンジルアクリレート、ベンジルメタクリレート、フェノキシアクリレート、フェノキシメタクリレート、イソボルニルアクリレート、イソボルニルメタクリレート、グリシジルメタクリレート、スチレン、 α -メチルスチレンアクリルアミド、メタアクリルアミド、アクリロニトリル、メタアクリロニトリルなどの単量体のうちの少なくとも1種の重合体）、エチレン-酢酸ビニル共重合体樹脂、ポリビニルブチラール、ポリビニルアルコール、プロピレングリコール、ウレタン系樹脂、メラミン系樹脂、フェノール樹脂などが挙げられる。

【0024】溶剤としては、例えば1価アルコールのうち高沸点のもの；エチレングリコールやグリセリンに代表されるジオールやトリオールなどの多価アルコール；アルコールをエーテル化および／またはエステル化した化合物（エチレングリコールモノアルキルエーテル、エチレングリコールジアルキルエーテル、エチレングリコールアルキルエーテルアセテート、ジエチレングリコールモノアルキルエーテルアセテート、ジエチレングリコールジアルキルエーテル、プロピレングリコールモノアルキルエーテル、プロピレングリコールジアルキルエーテル、プロピレングリコールアルキルアセテート）などが挙げられる。

【0025】以上のようにして得られる本発明の蛍光体ペーストを焼成した後に残存する蛍光体または本発明の蛍光体は、プラズマ曝露後の輝度が高い。PDPおよび希ガスランプの製造においては、蛍光体にバインダーを加えて溶媒と混合し（すなわち蛍光体ペーストにして）、発光部に塗布して500℃程度で熱処理してバインダーを除去することにより蛍光体を設置する工程が一般的であるが、本発明の蛍光体は、この熱処理後の輝度も高い。従って、本発明の蛍光体をPDPおよび希ガスランプなどの真空紫外線励起発光素子用に用いた場合、高輝度で寿命の長いPDPおよび希ガスランプが実現できるので、真空紫外線励起発光素子用として好適である。

【0026】本発明の蛍光体は真空紫外域以外の紫外線、X線および電子線などによっても励起可能であり、真空紫外域以外の紫外線、X線および電子線を励起源とした、蛍光灯、夜光表示、X線検査装置、CRTなどにも用いることができる。

【0027】

10

20

30

40

50

(5)

7

【実施例】次に、本発明を実施例によりさらに詳しく説明するが、本発明はこれらの実施例に限定されるものではない。以下の実施例、比較例において、蛍光体の輝度の測定は、 6.7 Pa ($5 \times 10^{-2}\text{ Torr}$) 以下の真空槽内で蛍光体にエキシマ 146 nm ランプ（ウシオ電機社製、H0012型）を用いて真空紫外線を照射して行った。

【0028】比較例1

青色蛍光体 $\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ （平均一次粒子径 $0.4\text{ }\mu\text{m}$ ）を空气中において 500°C で30分間保持して熱処理を行った後、圧力が 13.2 Pa で5体積% Xe －95体積% Ne の組成の雰囲気中に設置し、 50 W のプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定し、得られた輝度を100とした。

【0029】比較例2

青色蛍光体 $\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6$ （平均一次粒子径 $1.0\text{ }\mu\text{m}$ ）を、空气中において 500°C で30分間保持して熱処理を行った後、圧力が 13.2 Pa で5体積% Xe －95体積% Ne の組成の雰囲気中に設置し、 50 W のプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、得られた輝度は104であった。

【0030】実施例1

比較例2で用いた蛍光体と比較例1で用いた蛍光体とをそれぞれ本発明における蛍光物質A¹と蛍光物質B¹として用い、蛍光物質の重量比 $\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6/\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ が50/50になるように秤量し、エタノールを用いて湿式混合を行い、乾燥して得られた蛍光体を空气中において 500°C で30分間保持して熱処理を行った後、圧力が 13.2 Pa で5体積% Xe －95体積% Ne の組成の雰囲気中に設置し、 50 W のプラズマに15分間曝露さ

8

せた。蛍光体を取り出して輝度を測定した結果、青色に発光し、得られた輝度は127であった。

【0031】実施例2

比較例2で用いた蛍光体と比較例1で用いた蛍光体とをそれぞれ本発明における蛍光物質A¹と蛍光物質B¹として用い、蛍光物質の重量比 $\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6/\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ が80/20になるように秤量し、エタノールを用いて湿式混合を行い、乾燥して得られた蛍光体を空气中において 500°C で30分間保持して熱処理を行った後、圧力が 13.2 Pa で5体積% Xe －95体積% Ne の組成の雰囲気中に設置し、 50 W のプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、青色に発光し、得られた輝度は113であった。

【0032】実施例3

比較例2で用いた蛍光体と比較例1で用いた蛍光体とをそれぞれ本発明における蛍光物質A¹と蛍光物質B¹として用い、蛍光物質の重量比 $\text{Ca}_{0.9215}\text{Sr}_{0.0485}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_6/\text{Ba}_{0.9}\text{Eu}_{0.1}\text{MgAl}_{10}\text{O}_{17}$ が20/80になるように秤量し、エタノールを用いて湿式混合を行い、乾燥して得られた蛍光体を空气中において 500°C で30分間保持して熱処理を行った後、圧力が 13.2 Pa で5体積% Xe －95体積% Ne の組成の雰囲気中に設置し、 50 W のプラズマに15分間曝露させた。蛍光体を取り出して輝度を測定した結果、青色に発光し、得られた輝度は107であった。

【0033】

【発明の効果】本発明の蛍光体は、プラズマ曝露後の輝度が高く、特にPDPや希ガスランプなどの真空紫外線励起発光素子用に好適であり、高輝度で寿命の長い真空紫外線励起発光素子が実現できるので、工業的に極めて有用である。

フロントページの続き

Fターム(参考) 4H001 CA02 CA04 CA05 XA08 XA12
XA14 XA20 XA30 XA32 XA38
XA56 YA25 YA63

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] as the first component -- empirical formula $mM1 \cdot O \cdot nM2O \cdot 2M3O2$ ($M1$ in a formula -- calcium --) It is two or more sorts chosen from the group which consists of Sr and Ba, or calcium or Ba. $M2$ is one or more sorts chosen from the group which consists of Mg and Zn, $M3$ is one or more sorts chosen from the group which consists of Si and germanium, m is 3.5 or less [0.5 or more], and n is 2.5 or less [0.5 or more]. The fluorescent substance characterized by including the fluorescent material which consists of one or more sorts of activators chosen from the group which consists of the compound and Eu which are expressed, and Mn, and the fluorescent material which consists of an aluminate as the second component.

[Claim 2] The fluorescent substance according to claim 1 whose weight ratios of the first component / second component are 5 / 95 - 95/5.

[Claim 3] The fluorescent substance according to claim 1 or 2 whose first component is the fluorescent material which has the presentation expressed with empirical formula $(M11-aEua) (M21-bMnb) M32O6$ ($M1$, $M2$, and $M3$ in a formula have the same semantics as the above, and a is 0.5 or less [0 or more], and b is 0.5 or less [0 or more], and is $0 < a+b$).

[Claim 4] The fluorescent substance according to claim 1 to 3 whose first component is the fluorescent material which has the presentation expressed with empirical formula $calcium1-c-dSrcEudMgSi \cdot 2O6$ (c in a formula is 0.1 or less [0 or more], and d is 0.1 or less more greatly than 0.).

[Claim 5] the second component -- empirical formula $p(M41-eEue) O-q(M51-fMnf) O-rAl \cdot 2O3$ ($M4$ in a formula -- calcium --) It is one or more sorts chosen from the group which consists of Sr and Ba, and $M5$ is one or more sorts chosen from the group which consists of Mg and Zn. p is 1.5 or less [0.5 or more], q is 1.5 or less [0.5 or more], r is 5.5 or less [4.5 or more], e is 0.5 or less more greatly than 0, and f is 0.1 or less more greatly than 0. The fluorescent substance according to claim 1 to 4 which is the fluorescent material which has the presentation expressed.

[Claim 6] The fluorescent substance according to claim 1 to 5 whose second component is the fluorescent material which has the presentation expressed with empirical formula $Ba1-gEugMgAl \cdot 10O17$ (g in a formula is 0.3 or less more greatly than 0.).

[Claim 7] The fluorescent substance according to claim 1 to 6 one of whose first [an average of] particle diameter is 5 or less times of another first [an average of] particle diameter among the first component and the second component.

[Claim 8] The fluorescent substance according to claim 1 to 7 which is an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[Claim 9] The fluorescent substance paste characterized by including a fluorescent substance, a solvent, and a binder according to claim 1 to 8.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a fluorescent substance and a fluorescent substance paste.

[0002]

[Description of the Prior Art] The fluorescent substance is used for a fluorescent lamp, a noctilucence display, X-ray inspection equipment, CRT, a vacuum-ultraviolet-radiation excitation light emitting device, etc. It is objects for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display (PDP) and a rare-gas lamp, and the fluorescent substance which is excited by vacuum ultraviolet radiation and emits light is already known. For example, as a blue fluorescent substance, $\text{BO}_3\text{:Eu}$ whose $\text{Zn}_2\text{SiO}_4\text{:Mn}$ $\text{CaMgSi}_2\text{O}_6\text{:Eu}$ which is a silicate fluorescent substance is a borate fluorescent substance as a green fluorescent substance as a blue fluorescent substance (Y, Gd) is put in practical use as a red fluorescent substance, and $\text{BaMgAl}_{10}\text{O}_{17}\text{:Eu}$ which is an aluminate fluorescent substance is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp.

[0003]

However, since light was emitted by the light which a vacuum-ultraviolet-radiation excitation light emitting device generates the plasma by discharge in rare gas, irradiates the vacuum ultraviolet radiation emitted from the plasma at a fluorescent substance, excites a fluorescent substance, and is emitted from a fluorescent substance, the fluorescent substance was exposed to the plasma and had the problem that the brightness of the fluorescent substance after plasma exposure became low.

[0004]

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the fluorescent substance paste with which it comes to contain the fluorescent substance with high brightness and this fluorescent substance after plasma exposure.

[0005]

[Means for Solving the Problem] As a result of this invention persons' repeating research wholeheartedly that the above-mentioned technical problem should be solved under this situation, the fluorescent substance containing both the fluorescent material which consists of an aluminate, and the fluorescent material which consists of a silicate which has a specific presentation came to complete a header and this invention for the brightness after plasma exposure being high.

[0006] namely, this invention — as the first component — empirical formula $m\text{M}_1\text{O}-n\text{M}_2\text{O} \cdot 2\text{M}_3\text{O}_2$ (M_1 in a formula — calcium —) It is two or more sorts chosen from the group which consists of Sr and Ba, or calcium or Ba. M_2 is one or more sorts chosen from the group which consists of Mg and Zn, M_3 is one or more sorts chosen from the group which consists of Si and germanium, m is 3.5 or less [0.5 or more], and n is 2.5 or less [0.5 or more]. The fluorescent substance containing the fluorescent material which consists of one or more sorts of activators chosen from the group which consists of the compound and Eu which are expressed, and Mn, and the fluorescent material which consists of an aluminate as the second component is offered. Moreover, this invention offers the fluorescent substance paste containing the fluorescent substance, solvent, and binder of the above-mentioned publication.

[0007]

[Embodiment of the Invention] This invention is explained in detail below. The fluorescent substance of this invention contains the fluorescent material (it may be called "a fluorescent material A1" below) which one or more sorts chosen from the group which becomes the compound expressed with empirical formula $m\text{M}_1\text{O}-n\text{M}_2\text{O} \cdot 2\text{M}_3\text{O}_2$ from Eu and Mn as an activator come to contain. M_1 in said formula is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or calcium or Ba. M_2 is one or more sorts chosen from the group which consists of Mg and Zn. M_3 is one or more sorts chosen from the group which consists of Si and germanium. m is 3.5 or less [0.5 or more], and n is 2.5 or less [0.5 or more]. m and n — the above — the brightness of the fluorescent substance after plasma exposure becomes it low that it is out of range.

[0008] As a fluorescent material A1, it is empirical formula $(\text{M}_{11}-a\text{Eua}) (\text{M}_{21}-b\text{Mnb}) \text{M}_3\text{O}_6$ (M_1 , M_2 , and M_3 in a formula have the same semantics as the above). a is 0.5 or less [0 or more], and b is 0.5 or less [0 or more], and is $0 < a+b$. The fluorescent material which has the presentation expressed is desirable still more desirable, and it is empirical formula calcium $1-c-d\text{SrcEuMgSi } 2\text{O}_6$ (c in a formula is 0.1 or less [0 or more], and d is 0.1 or less more greatly than 0.). It is the fluorescent material which has the presentation expressed.

[0009] The fluorescent material (it may be called "a fluorescent material B1" below) which consists of an aluminate is included in the fluorescent substance of this invention besides the above A1. although it will not be limited especially if it is the fluorescent substance which consists of an aluminate — empirical formula $p(\text{M}_{41}-e\text{Eue}) \text{O}-q(\text{M}_{51}-f\text{Mnf}) \text{O}-r\text{Al } 2\text{O}_3$ (M_4 in a formula — calcium —) It is one or more sorts chosen from the group which consists of Sr and Ba, and M_5 is one or more sorts chosen from the group which consists of Mg and Zn. p is 1.5 or less [0.5 or more], r is 5.5 or less [4.5 or more], e is 0.5 or less more greatly than 0, and f is 0.1 or less more greatly than 0. The fluorescent material which has the presentation expressed (it may be called "fluorescent material B-2" below) It is desirable and the fluorescent material which has the presentation expressed with empirical formula $\text{Ba}_1-g\text{EugMgAl } 10\text{O}_{17}$ (g in a formula is 0.3 or less more greatly than 0.) is still more desirable.

[0010] In the fluorescent substance of this invention, the weight ratio of the fluorescent material A1-/fluorescent material B1 has the desirable range of 5 / 95 – 95/5, its range of 20 / 80 – 90/10 is still more desirable, and its range of 30 / 70 – 85/15 is still more desirable. There is a possibility that the brightness after plasma exposure may become low when smaller than 95/5 when the weight ratio of the fluorescent material A1-/fluorescent material B1 is larger

than 5/95.

[0011] Moreover, it is desirable that the first [an average of] particle diameter of one of fluorescent materials is 5 or less times of the first [an average of] particle diameter of another fluorescent material among a fluorescent material A1 and a fluorescent material B1.

[0012] Next, the manufacture approach of the fluorescent substance of this invention is explained. The fluorescent substance of this invention can be obtained by mixing a fluorescent material A1 and a fluorescent material B1. Especially as an approach of mixing, although not limited, the stirring method usually used industrially, the ball mill method, the 3 roll-mill method, etc. can be illustrated. Moreover, fluorescent substances other than A1 and B1 may be mixed.

[0013] Here, a fluorescent material A1 is the mixture of metallic compounds, and can be manufactured by calcinating the mixture which can serve as a fluorescent material A1 by baking. the compound which decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide as the source of calcium for manufacturing a fluorescent material A1, the source of strontium, and a source of barium — or the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of magnesium, and a source of zinc, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of silicon, and a source of germanium, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the europium used as an activator, and a raw material containing manganese, the oxide of a high grade (99% or more) can be used.

[0014] A fluorescent material A1 can be manufactured by carrying out weighing capacity, blending, mixing and calcinating the above-mentioned compound so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing of these compounds. After mixing, the fluorescent material A1 in this invention is obtained by calcinating in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When the compound which decomposes at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide is used, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement.

[0015] Especially as a firing environments for manufacturing a fluorescent material A1, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1-10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air ambient atmosphere and a reducing atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0016] Furthermore, the fluorescent material A1 obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the obtained fluorescent material A1.

[0017] Next, the manufacture approach of the fluorescent material B1 in this invention is explained. Although especially the manufacture approach of a fluorescent material B1 is not limited, it is the mixture of metallic compounds and can manufacture by calcinating the mixture which can serve as a fluorescent material which consists of an aluminate by baking. For example, in order to obtain the mixture of the metallic compounds for manufacturing fluorescent material B-2 which has a desirable presentation among fluorescent materials B1, or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of barium, the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of magnesium, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of aluminum, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material containing the europium used as an activator, the oxide of a high grade (99% or more) can be used. The mixture of metallic compounds is obtained by carrying out weighing capacity and mixing the above-mentioned compound so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing.

[0018] A fluorescent material B1 is obtained by calcinating the mixture of metallic compounds in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When the compound which decomposes at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide is used, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement.

[0019] Especially as a firing environments for manufacturing a fluorescent material B1, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1-10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air ambient atmosphere and a reducing atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0020] Furthermore, the fluorescent material B1 obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the fluorescent substance obtained.

[0021] Next, the fluorescent substance paste of this invention is explained. When the fluorescent substance paste of this invention can be used like the conventional fluorescent substance paste and calcinated including the fluorescent substance, solvent, and binder of this invention, it is a fluorescent substance paste with which the fluorescent substance of this invention remains.

[0022] The fluorescent substance paste of this invention can be manufactured by the well-known approach using a well-known binder and a well-known solvent. For example, a fluorescent material A1, a fluorescent material B1, a binder, and a solvent can be obtained by mixing using a ball mill, 3 roll mills, etc.

[0023] as a binder — cellulose type resin (ethyl cellulose and methyl cellulose —) A nitrocellulose, an acetyl cellulose, cellulose propionate, Hydroxypropylcellulose, butyl cellulose, benzyl cellulose, acrylic resin (an acrylic acid and a methacrylic acid —), such as a denaturation cellulose Methyl acrylate, methyl methacrylate, ethyl acrylate, Ethyl methacrylate, propylacrylate, propyl methacrylate, Isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, N-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, Benzyl acrylate, benzyl methacrylate, phenoxy acrylate, Phenoxy methacrylate, isobornyl acrylate, isobornyl methacrylate, Glycidyl methacrylate, styrene, alpha-methyl-styrene acrylamide, At least one sort of polymers of the monomers, such as meta-acrylamide, acrylonitrile, and meta-acrylonitrile, Ethylene-vinylacetate copolymer resin, a polyvinyl butyral, polyvinyl alcohol, propylene glycol, urethane system resin, melamine system resin, phenol resin, etc. are mentioned.

[0024] the compound (ethylene glycol monoalkyl ether —) which etherified and/or esterified as a solvent polyhydric-alcohol; alcohol, such as diol represented by thing; ethylene glycol and the glycerol of a high-boiling point, for example among monohydric alcohol, and triol Ethylene glycol dialkyl ether, ethylene glycol alkyl ether acetate, Diethylene-glycol monoalkyl ether acetate, the diethylene-glycol dialkyl ether, propylene glycol monoalkyl ether, the propylene glycol dialkyl ether, propylene glycol alkyl acetate, etc. are mentioned.

[0025] The fluorescent substance which remains after calcinating the fluorescent substance paste of this invention obtained as mentioned above, or the fluorescent substance of this invention has the high brightness after plasma exposure, in manufacture of PDP and a rare-gas lamp, although the process which installs a fluorescent substance by adding a binder to a fluorescent substance, mixing with a solvent (namely, a fluorescent substance paste — carrying out), applying to a light-emitting part, heat-treating at about 500 degrees C, and removing a binder is common, the brightness after this heat treatment of the fluorescent substance of this invention is also high. Therefore, since long PDP and the long rare-gas lamp of a life can be realized by high brightness when the fluorescent substance of this invention is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, it is suitable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0026] The fluorescent substance of this invention can be excited with ultraviolet rays, X-rays, electron rays, etc. other than a vacuum ultraviolet area, and can be used for the fluorescent lamp and noctilucence display which made the ultraviolet rays, X-rays, and electron rays other than a vacuum ultraviolet area the source of excitation, X-ray inspection equipment, CRT, etc.

[0027]

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples. In the following examples and the example of a comparison, measurement of the brightness of a fluorescent substance was performed by using an excimer 146nm lamp (the USHIO, INC. make, H0012 mold) for a fluorescent substance within the vacuum tub below 6.7Pa (5x10⁻²Torr), and irradiating vacuum ultraviolet radiation.

[0028] After heat-treating by holding example of comparison 1 blue fluorescent substance Ba_{0.9}Eu_{0.1}MgAl 10017 (first [an average of] particle diameter of 0.4 micrometers) for 30 minutes at 500 degrees C in air, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. The fluorescent substance was taken out, brightness was measured and the obtained brightness was set to 100.

[0029] After heat-treating by holding for 30 minutes at 500 degrees C in air, the pressure installed example of comparison 2 blue fluorescent substance calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi₂O₆ (first [an average of] particle diameter of 1.0 micrometers) into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it expose to the plasma of 50W for 15 minutes. The obtained brightness was 104, as a result of taking out a fluorescent substance and measuring brightness.

[0030] The fluorescent substance used in the example 2 of example 1 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O₆/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi₂(s)0.1MgAl 10017 of a fluorescent material may become 50/50. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 127.

[0031] The fluorescent substance used in the example 2 of example 2 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O₆/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi₂(s)0.1MgAl 10017 of a fluorescent material may become 80/20. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 113.

[0032] The fluorescent substance used in the example 2 of example 3 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O₆/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi₂(s)0.1MgAl 10017 of a fluorescent material may become 20/80. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 107.

[0033]

[Effect of the Invention] The brightness after plasma exposure is high, and the fluorescent substance of this invention is especially suitable for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, and since it can realize the long vacuum-ultraviolet-radiation excitation light emitting device of a life by high brightness, it is very useful industrially.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to a fluorescent substance and a fluorescent substance paste.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] The fluorescent substance is used for a fluorescent lamp, a noctilucence display, X-ray inspection equipment, CRT, a vacuum-ultraviolet-radiation excitation light emitting device, etc. It is objects for vacuum-ultraviolet-radiation excitation light emitting devices, such as a plasma display (PDP) and a rare-gas lamp, and the fluorescent substance which is excited by vacuum ultraviolet radiation and emits light is already known. For example, as a blue fluorescent substance, BO₃:Eu whose Zn₂SiO₄:Mn CaMgSi₂O₆:Eu which is a silicate fluorescent substance is a borate fluorescent substance as a green fluorescent substance as a blue fluorescent substance (Y, Gd) is put in practical use as a red fluorescent substance, and BaMgAl₁₀O₁₇:Eu which is an aluminate fluorescent substance is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp. [0003] However, since light was emitted by the light which a vacuum-ultraviolet-radiation excitation light emitting device generates the plasma by discharge in rare gas, irradiates the vacuum ultraviolet radiation emitted from the plasma at a fluorescent substance, excites a fluorescent substance, and is emitted from a fluorescent substance, the fluorescent substance was exposed to the plasma and had the problem that the brightness of the fluorescent substance after plasma exposure became low.

[Translation done.]

* NOTICES *

JPO and NCIP I are not responsible for any
damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] The brightness after plasma exposure is high, and the fluorescent substance of this invention is especially suitable for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, and since it can realize the long vacuum-ultraviolet-radiation excitation light emitting device of a life by high brightness, it is very useful industrially.

[Translation done.]

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention is to offer the fluorescent substance paste with which it comes to contain the fluorescent substance with high brightness and this fluorescent substance after plasma exposure.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] As a result of this invention persons' repeating research wholeheartedly that the above-mentioned technical problem should be solved under this situation, the fluorescent substance containing both the fluorescent material which consists of an aluminate, and the fluorescent material which consists of a silicate which has a specific presentation came to complete a header and this invention for the brightness after plasma exposure being high.

[0006] namely, this invention — as the first component — empirical formula $mM1 O-nM2O.2M3O2$ (M1 in a formula — calcium —) It is two or more sorts chosen from the group which consists of Sr and Ba, or calcium or Ba. M2 is one or more sorts chosen from the group which consists of Mg and Zn, M3 is one or more sorts chosen from the group which consists of Si and germanium, m is 3.5 or less [0.5 or more], and n is 2.5 or less [0.5 or more]. The fluorescent substance containing the fluorescent material which consists of one or more sorts of activators chosen from the group which consists of the compound and Eu which are expressed, and Mn, and the fluorescent material which consists of an aluminate as the second component is offered. Moreover, this invention offers the fluorescent substance paste containing the fluorescent substance, solvent, and binder of the above-mentioned publication.

[0007]

[Embodiment of the Invention] This invention is explained in detail below. The fluorescent substance of this invention contains the fluorescent material (it may be called "a fluorescent material A1" below) which one or more sorts chosen from the group which becomes the compound expressed with empirical formula $mM1 O-nM2O.2M3O2$ from Eu and Mn as an activator come to contain. M1 in said formula is two or more sorts chosen from the group which consists of calcium, Sr, and Ba, or calcium or Ba. M2 is one or more sorts chosen from the group which consists of Mg and Zn. M3 is one or more sorts chosen from the group which consists of Si and germanium, m is 3.5 or less [0.5 or more], and n is 2.5 or less [0.5 or more]. m and n — the above — the brightness of the fluorescent substance after plasma exposure becomes it low that it is out of range.

[0008] As a fluorescent material A1, it is empirical formula $(M11-aEua) (M21-bMnb) M32O6$ (M1, M2, and M3 in a formula have the same semantics as the above). a is 0.5 or less [0 or more], and b is 0.5 or less [0 or more], and is $0 < a+b$. The fluorescent material which has the presentation expressed is desirable still more desirable, and it is empirical formula $calcium1-c-dSrcEudMgSi 2O6$ (c in a formula is 0.1 or less [0 or more], and d is 0.1 or less more greatly than 0.). It is the fluorescent material which has the presentation expressed.

[0009] The fluorescent material (it may be called "a fluorescent material B1" below) which consists of an aluminate is included in the fluorescent substance of this invention besides the above A1. although it will not be limited especially if it is the fluorescent substance which consists of an aluminate — empirical formula $p(M41-eEue) O-q(M51-fMnf) O-rAl 2O3$ (M4 in a formula — calcium —) It is one or more sorts chosen from the group which consists of Sr and Ba, and M5 is one or more sorts chosen from the group which consists of Mg and Zn. p is 1.5 or less [0.5 or more], q is 1.5 or less [0.5 or more], r is 5.5 or less [4.5 or more], e is 0.5 or less more greatly than 0, and f is 0.1 or less more greatly than 0. The fluorescent material which has the presentation expressed (it may be called "fluorescent material B-2" below) It is desirable and the fluorescent material which has the presentation expressed with empirical formula $Ba1-gEugMgAl 10O17$ (g in a formula is 0.3 or less more greatly than 0.) is still more desirable.

[0010] In the fluorescent substance of this invention, the weight ratio of the fluorescent material A1-/fluorescent material B1 has the desirable range of $5 / 95 - 95/5$, its range of $20 / 80 - 90/10$ is still more desirable, and its range of $30 / 70 - 85/15$ is still more desirable. There is a possibility that the brightness after plasma exposure may become low when smaller than $95/5$ when the weight ratio of the fluorescent material A1-/fluorescent material B1 is larger than $5/95$.

[0011] Moreover, it is desirable that the first [an average of] particle diameter of one of fluorescent materials is 5 or less times of the first [an average of] particle diameter of another fluorescent material among a fluorescent material A1 and a fluorescent material B1.

[0012] Next, the manufacture approach of the fluorescent substance of this invention is explained. The fluorescent substance of this invention can be obtained by mixing a fluorescent material A1 and a fluorescent material B1. Especially as an approach of mixing, although not limited, the stirring method usually used industrially, the ball mill method, the 3 roll-mill method, etc. can be illustrated. Moreover, fluorescent substances other than A1 and B1 may be mixed.

[0013] Here, a fluorescent material A1 is the mixture of metallic compounds, and can be manufactured by calcinating the mixture which can serve as a fluorescent material A1 by baking. the compound which decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide as the source of calcium for manufacturing a fluorescent material A1, the source of strontium, and a source of barium — or the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of magnesium, and a source of zinc, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the source of silicon, and a source of germanium, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as the europium used as an activator, and a raw material containing manganese, the oxide of a high grade (99% or more) can be used.

[0014] A fluorescent material A1 can be manufactured by carrying out weighing capacity, blending, mixing and calcinating the above-mentioned compound so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing of these compounds. After mixing, the fluorescent material A1 in this invention is obtained by calcinating in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When the compound which decomposes at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide is used, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement.

[0015] Especially as a firing environments for manufacturing a fluorescent material A1, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1-10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air ambient atmosphere and a reducing atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0016] Furthermore, the fluorescent material A1 obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the obtained fluorescent material A1.

[0017] Next, the manufacture approach of the fluorescent material B1 in this invention is explained. Although especially the manufacture approach of a fluorescent material B1 is not limited, it is the mixture of metallic compounds and can manufacture by calcinating the mixture which can serve as a fluorescent material which consists of an aluminate by baking. For example, in order to obtain the mixture of the metallic compounds for manufacturing fluorescent material B-2 which has a desirable presentation among fluorescent materials B1, or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of barium, the oxide of a high grade (99.9% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of magnesium, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a source of aluminum, the oxide of a high grade (99% or more) can be used. Or it decomposes at elevated temperatures, such as a hydroxide of a high grade (99% or more), a carbonate, a nitrate, a halogenide, and an oxalate, and cannot become an oxide as a raw material containing the europium used as an activator, the oxide of a high grade (99% or more) can be used. The mixture of metallic compounds is obtained by carrying out weighing capacity and mixing the above-mentioned compound so that it may become a predetermined presentation. The ball mill usually used industrially, a V shaped rotary mixer, or stirring equipment can be used for mixing.

[0018] A fluorescent material B1 is obtained by calcinating the mixture of metallic compounds in a 1000 to 1500 degrees C temperature requirement for 1 to 100 hours. When the compound which decomposes at elevated temperatures, such as a hydroxide, a carbonate, a nitrate, a halogenide, and an oxalate, and can turn into an oxide is used, it is also possible to carry out temporary quenching before this baking in a 600 to 900 degrees C temperature requirement.

[0019] Especially as a firing environments for manufacturing a fluorescent material B1, although not limited, it is desirable to calcinate hydrogen by the reducing atmosphere of the nitrogen 0.1-10 volume % Included, an argon, etc., for example. Moreover, any of an atmospheric-air-ambient-atmosphere-and-a-reducing-atmosphere are sufficient as the ambient atmosphere of temporary quenching. Moreover, in order to promote a reaction, the flux of optimum dose may be added.

[0020] Furthermore, the fluorescent material B1 obtained by the above-mentioned approach can be ground using a ball mill, a jet mill, etc. Moreover, it can wash and classify. Re-baking can also be performed in order to raise the crystallinity of the fluorescent substance obtained.

[0021] Next, the fluorescent substance paste of this invention is explained. When the fluorescent substance paste of this invention can be used like the conventional fluorescent substance paste and calcinated including the fluorescent substance, solvent, and binder of this invention, it is a fluorescent substance paste with which the fluorescent substance of this invention remains.

[0022] The fluorescent substance paste of this invention can be manufactured by the well-known approach using a well-known binder and a well-known solvent. For example, a fluorescent material A1, a fluorescent material B1, a binder, and a solvent can be obtained by mixing using a ball mill, 3 roll mills, etc.

[0023] as a binder -- cellulose type resin (ethyl cellulose and methyl cellulose --) A nitrocellulose, an acetyl cellulose, cellulose propionate, Hydroxypropylcellulose, butyl cellulose, benzyl cellulose, acrylic resin (an acrylic acid and a methacrylic acid --), such as a denaturation cellulose Methyl acrylate, methyl methacrylate, ethyl acrylate, Ethyl methacrylate, propylacrylate, propyl methacrylate, Isopropyl acrylate, isopropyl methacrylate, n-butyl acrylate, N-butyl methacrylate, tert-butyl acrylate, tert-butyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, Benzyl acrylate, benzyl methacrylate, phenoxy acrylate, Phenoxy methacrylate, isobornyl acrylate, isobornyl methacrylate, Glycidyl methacrylate, styrene, alpha-methyl-styrene acrylamide, At least one sort of polymers of the monomers, such as meta-acrylamide, acrylonitrile, and meta-acrylonitrile, Ethylene-vinylacetate copolymer resin, a polyvinyl butyral, polyvinyl alcohol, propylene glycol, urethane system resin, melamine system resin, phenol resin, etc. are mentioned.

[0024] the compound (ethylene glycol monoalkyl ether --) which etherified and/or esterified as a solvent polyhydric-alcohol; alcohol, such as diol represented by thing; ethylene glycol and the glycerol of a high-boiling point, for example among monohydric alcohol, and triol Ethylene glycol dialkyl ether, ethylene glycol alkyl ether acetate, Diethylene-glycol monoalkyl ether acetate, the diethylene-glycol dialkyl ether, propylene glycol monoalkyl ether, the propylene glycol dialkyl ether, propylene glycol alkyl acetate, etc. are mentioned.

[0025] The fluorescent substance which remains after calcinating the fluorescent substance paste of this invention obtained as mentioned above, or the fluorescent substance of this invention has the high brightness after plasma exposure. in manufacture of PDP and a rare-gas lamp, although the process which installs a fluorescent substance by adding a binder to a fluorescent substance, mixing with a solvent (namely, a fluorescent substance paste -- carrying out), applying to a light-emitting part, heat-treating at about 500 degrees C, and removing a binder is common, the brightness after this heat treatment of the fluorescent substance of this invention is also high. Therefore, since long PDP and the long rare-gas lamp of a life can be realized by high brightness when the fluorescent substance of this

invention is used for vacuum-ultraviolet-radiation excitation light emitting devices, such as PDP and a rare-gas lamp, it is suitable as an object for vacuum-ultraviolet-radiation excitation light emitting devices.

[0026] The fluorescent substance of this invention can be excited with ultraviolet rays, X-rays, electron rays, etc. other than a vacuum ultraviolet area, and can be used for the fluorescent lamp and noctilucence display which made the ultraviolet rays, X-rays, and electron rays other than a vacuum ultraviolet area the source of excitation, X-ray inspection equipment, CRT, etc.

[0027]

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Next, although an example explains this invention in more detail, this invention is not limited to these examples. In the following examples and the example of a comparison, measurement of the brightness of a fluorescent substance was performed by using an excimer 146nm lamp (the USHIO, INC. make, H0012 mold) for a fluorescent substance within the vacuum tub below 6.7Pa (5×10^{-2} Torr), and irradiating vacuum ultraviolet radiation.

[0028] After heat-treating by holding example of comparison 1 blue fluorescent substance Ba_{0.9}Eu_{0.1}MgAl 10017 (first [an average of] particle diameter of 0.4 micrometers) for 30 minutes at 500 degrees C in air, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. The fluorescent substance was taken out, brightness was measured and the obtained brightness was set to 100.

[0029] After heat-treating by holding for 30 minutes at 500 degrees C in air, the pressure installed example of comparison 2 blue fluorescent substance calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi 2O6 (first [an average of] particle diameter of 1.0 micrometers) into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it expose to the plasma of 50W for 15 minutes. The obtained brightness was 104, as a result of taking out a fluorescent substance and measuring brightness.

[0030] The fluorescent substance used in the example 2 of example 1 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O6/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi(s)_{0.1}MgAl 10017 of a fluorescent material may become 50/50. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 127.

[0031] The fluorescent substance used in the example 2 of example 2 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O6/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi(s)_{0.1}MgAl 10017 of a fluorescent material may become 80/20. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 113.

[0032] The fluorescent substance used in the example 2 of example 3 comparison and the fluorescent substance used in the example 1 of a comparison are used as the fluorescent material A1 in this invention, and a fluorescent material B1, respectively. Weighing capacity is carried out so that 2O6/Ba_{0.9}Eu of weight ratio calcium_{0.9215}Sr_{0.0485}Eu_{0.03}MgSi(s)_{0.1}MgAl 10017 of a fluorescent material may become 20/80. After heat-treating by holding in air the fluorescent substance which performed wet blending and was obtained by drying using ethanol for 30 minutes at 500 degrees C, the pressure installed into the ambient atmosphere of a presentation of 5 volume %Xe-95 volume %Ne by 13.2Pa, and made it exposed to the plasma of 50W for 15 minutes. As a result of taking out a fluorescent substance and measuring brightness, light was emitted blue and the obtained brightness was 107.

[Translation done.]